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Molecular Engineering of Liquid-crystalline Polymers by Living Polymerization. 18. s_C^* Mesophase in Copolymers of (2S, 3S)-(+)-2-Chloro-3-Methylpentyl 4'-(ω-Vinyloxyalkyloxy) biphenyl-4-carboxylate with Undecanyl and Octyl Alkyl Groups

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The synthesis and living cationic polymerization of (2S, 3S)-(+)-2-chloro-3-methylpentyl 4'-(11-vinyloxyundecanyloxy)biphenyl-4-carboxylate (15-11) and (2S, 3S)-(+)-2-chloro-3-methylpentyl 4'-(8-vinyloxyoctyloxy)biphenyl-4-carboxylate (15-8) are described. Poly(15-11)s and poly(15-8)s with degrees of polymerization (DP) up to 25 and polydispersities lower than 1.15 were synthesized and characterized by differential scanning calorimetry (DSC) and thermal optical polarized microscopy. Over the entire range of molecular weights poly(15-11)s and poly(15-8)s exhibit enantiotropic smectic A (s_A) and chiral smectic C (s_C*) mesophases. In addition, all poly(15-11)s exhibit a crystalline phase. Poly(15-8)s are noncrystallizable. However, poly(15-8)s with degrees of polymerization higher than 12 exhibit an unidentified s_X mesophase. Poly(15-11-co-15-8)X/Y (where X/Y represents the molar ratio of monomer 15-11 to monomer 15-8) with DP of about 15 and polydispersities lower than 1.11 were also synthesized and characterized. Both the s_A and s_C* mesophases of these copolymers exhibit continuous dependences of composition.

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ABSTRACT

The synthesis and living cationic polymerization of (2S, 3S)-(+)-2-chloro-3-methylpentyl 4'-(11-vinyloxyundecanyloxy)biphenyl-4-carboxylate (15-11) and (2S, 3S)-(+)-2-chloro-3-methylpentyl 4'-(8-vinyloxyoctyloxy)biphenyl-4-carboxylate (15-8) are described. Poly(15-11)s and poly(15-8)s with degrees of polymerization (DP) up to 25 and polydispersities lower than 1.15 were synthesized and characterized by differential scanning calorimetry (DSC) and thermal optical polarized microscopy. Over the entire range of molecular weights poly(15-11)s and poly(15-8)s exhibit enantiotropic smectic A (s_A) and chiral smectic C (s_C^*) mesophases. In addition, all poly(15-11)s exhibit a crystalline phase. Poly(15-8)s are noncrystallizable. However, poly(15-8)s with degrees of polymerization higher than 12 exhibit an unidentified s_X mesophase. Poly(15-11-co-15-8)X/Y (where X/Y represents the molar ratio of monomer 15-11 to monomer 15-8) with DP of about 15 and polydispersities lower than 1.11 were also synthesized and characterized. Both the s_A and s_C^* mesophases of these copolymers exhibit continuous dependences of composition.

Keywords: living cationic polymerization and copolymerization; chiral smectic C mesophase; vinyl ether.

INTRODUCTION

Since the first examples of mesogenic vinyl ethers and liquid crystalline poly(vinyl ether)s were reported from our laboratory[1], several other research groups became actively involved in the synthesis of mesomorphic poly(vinyl ether)s mainly because they can be polymerized by a living cationic mechanism and thus lead to polymers with well controlled molecular weight and narrow polydispersity[2-4].

In the previous publications from our research group we have reported the synthesis and living cationic polymerization of ω-[(4-cyano-4'-biphenyl)oxy]alkyl vinyl ethers with alkyl groups from ethyl to undecanyl[5] and of other mesogenic vinyl ethers containing functional groups such as double bond, triple bond and crown ether[6]. The influence of molecular weight on the mesomorphic behavior of these poly(vinyl ether)s was discused[5]. The first series of side chain liquid crystalline copolymers of various composition with constant molecular weight and narrow polydispersity were also prepared from these vinyl ethers via a living cationic copolymerization[6c,6e,7]. All these experiments have shown that living cationic polymerization can provide a quantitative approach to the molecular engineering of side chain

liquid crystalline copolymers exhibiting uniaxial nematic, various smectic and reentrant nematic mesophases[6,7a-d,7e].

Since Meyer[8] predicted that compounds exhibiting a chiral smectic C (sC^*) mesophase should be ferroelectric, several different laboratories have been interested in the study of side chain liquid crystalline polymers exhibiting a sC^* mesophase[9-20]. Presently, there is very little understanding of molecular design of side chain liquid crystalline polymers displaying a sC^* mesophase, and of the influence of various architectural parameters of these polymers on their dynamics[9-21].

We are interested in the molecular engineering of side chain liquid crystalline polymers exhibiting a sC^* mesophase[22]. In previous publications[22a,b] from this series we have described the synthesis and living cationic polymerizations of S-(-)-2-methylbutyl 4'-(ω-vinyloxyalkyloxy)biphenyl-4-carboxylate with undecanyl[22a], octyl[22b] and hexyl[22a] alkyl groups. The mesomorphic behavior of these polymers was discussed as a function of molecular weight and spacer length. Copolymers of various composition with constant molecular weight and narrow molecular weight distribution were also synthesized by living cationic polymerization[22b]. These copolymerization experiments allowed the synthesis of copolymers exhibiting sC^* mesophase from below 10 °C up to 50-80 °C.

In this paper, we will describe the synthesis, living cationic polymerization and copolymerization of (2S, 3S)-(+)-2-chloro-3-methylpentyl 4'-(ω-vinyloxyalkyloxy)biphenyl-4-carboxylate with undecanyl and octyl alkyl groups. The mesomorphic behavior of these polymers will be discussed as a function of molecular weight and copolymer composition.

EXPERIMENTAL

Materials

4-Hydroxybiphenyl (97%), dimethylsulfate (99%+), HBr (48%), 11-bromoundecan-1-ol (98%), 8-bromooctanoic acid (97%), borane-tetrahydrofuran, n-butyl vinyl ether (98%), tetra-n-butylammonium hydrogen sulfate (TBAH), L-isoleucine [(2S, 3S)-(+)-2-amino-3-methylpentanoic acid, $[\alpha]^{20}$=+41°C (c=4, 6 N HCl)] (99%) and dimethyl sulfoxide (anhydrous, 99%+, packaged under nitrogen in sure/seal bottle) (all from Aldrich), 1,10-phenanthroline (anhydrous, 99%), palladium (II) diacetate (both from Lancaster Synthesis) and acetyl chloride (99%) (from Fluka) were used as received. Methylene chloride (from Fisher) was purified by washing with concentrated sulfuric acid several times until the acid layer remains colorless, then with water, dried over anhydrous $MgSO_4$, refluxed over calcium hydride and freshly

distilled under argon before each use. Trifluoromethanesulfonic acid (triflic acid, 98%, from Aldrich) was distilled under vacuum.

Techniques

^{1}H-NMR (200 MHz) spectra were recorded on a Varian XL-200 spectrometer. Infrared (IR) spectra were recorded on a Perkin-Elmer 1320 infrared spectrophotometer. Relative molecular weights of polymers were measured by gel permeation chromatography (GPC) with a Perkin-Elmer Series 10 LC instrument equipped with LC-100 column oven and a Nelson Analytical 900 series integrator data station. A set of two Perkin-Elmer PL gel columns of $5x10^2$ and 10^4 Å with $CHCl_3$ as solvent (1ml/min) were used. The measurements were made at 40 °C using the UV detector. Polystyrene standards were used for the calibration plot. High pressure liquid chromatography (HPLC) experiments were performed with the same instrument. A Perkin-Elmer DSC-4 differential scanning calorimeter equipped with a TADS data station was used to determine the thermal transition temperatures which were reported as the maxima and minima of their endothermic and exothermic peaks. In all cases, heating and cooling rates were 20 °C/min. Glass transition temperatures (T_g) were read at the middle of the change in the heat capacity. A Carl-Zeiss optical polarized microscope (magnification 100x) equipped with a Mettler FP 82 hot stage and a Mettler FP 80 central processor was used to observe the thermal transitions and to verify the anisotropic textures.

Synthesis of (2S, 3S)-(+)-2-Chloro-3-Methylpentyl 4'-(11-Vinyloxyundecanyloxy)biphenyl-4-carboxylate (15-11) and (2S, 3S)-(+)-2-Chloro-3-Methylpentyl 4'-(8-Vinyloxyoctyloxy) biphenyl-4-carboxylate (15-8)

Both monomers 15-11 and 15-8 were synthesized according to Scheme I. The synthesis of compounds 6, 7, 8, 9, 10, 13 and 14 was described previously[22a,b].

(2S, 3S)-(+)-2-Chloro-3-Methylpentanoic Acid (2)[23]

L-Isoleucine [(2S, 3S)-(+)-2-amino-3-methylpentanoic acid] (26.23 g, 0.2 mol) was dissolved in a mixture of 125 ml concentrate HCl, 90 ml H_2O and 120 ml 1,4-dioxane. After the solution was cooled to 0-5 °C, a solution of $NaNO_2$ (22 g, 0.3 mol.) in 40 ml H_2O was added slowly during about 2 hours. After being stirred for 4 additional hours at a temperature below 5 °C, the reaction mixture was extracted with 400 ml diethyl ether in 4 portions. The combined ether extract was washed with 5% aqueous $NaHCO_3$ and H_2O, and dried over anhydrous $MgSO_4$. The solvent was removed by a rotary evaporator, and the remained

product was distilled at reduced pressure to give 19.1 g (64%) of colorless liquid (b.p. 92.0-96.0 °C/5.0 mmHg). ^{1}H-NMR ($CDCl_3$, TMS, δ, ppm): 0.94 (t, 3H, $C\underline{H}_3CH_2$-), 1.09 (d, 3H, $C\underline{H}_3CH(CH_2CH_3)$-), 1.33 and 1.64 (2m, 2H, $CH_3C\underline{H}_2$-), 2.12 (m, 1H, $CH_3CH_2C\underline{H}(CH_3)$-), 4.24 (d, 1H, -C<u>H</u>(Cl)-), 9.98 (s, 1H, -COO<u>H</u>).

(2S, 3S)-(+)-2-Chloro-3-Methyl-1-Pentanol (3)

To a solution of $LiAlH_4$ (4.1 g, 0.103 mol) in 250 ml diethyl ether cooled in an ice bath was added compound 2 (15.5 g, 0.103 mol) during about 2 hours. The reaction mixture was then heated to reflux overnight. After the excess $LiAlH_4$ was destroyed by dilute HCl, the product was extracted with diethyl ether several times. The combined ether solution was washed with H_2O and dried over anhydrous $MgSO_4$. Diethyl ether was then removed by a rotary evaporator and the resulted liquid was distilled under vacuum to yield 9.9 g of a colorless liquid (70%), b.p. 57.0-59.0 °C/4.0 mmHg). ^{1}H-NMR ($CDCl_3$, TMS, δ, ppm): 0.90 (t, 3H, $C\underline{H}_3CH_2$-), 1.03 (d, 3H, $C\underline{H}_3CH(CH_2CH_3)$-), 1.35 and 1.63 (2m, 2H, $CH_3C\underline{H}_2$-), 1.83 (m, 1H, $CH_3CH_2C\underline{H}(CH_3)$-), 1.97 (s, 1H, -$CH_2O\underline{H}$), 3.59-3.84 (m, 2H, -$C\underline{H}_2OH$), 3.98 (d, 1H, -C<u>H</u>(Cl)-).

(2S, 3S)-(+)-2-Chloro-3-Methylpentyl Toluene-p-sulphonate (4)

Compound 3 (5 g, 0.0366 mol) was added slowly to a solution of p-toluenesulfonyl chloride (13.95 g, 0.0732 mol) in 30 ml dry pyridine at 0 °C within one hour. After it was stirred at room temperature overnight the reaction mixture was poured into 50 ml H_2O and the product was extracted with diethyl ether 4 times. The combined ether solution was washed with dilute HCl and H_2O, and then was dried over anhydrous $MgSO_4$. Diethyl ether was removed by a rotary evaporator to give a light yellow liquid, which was purified by column chromatography (silica gel, CH_2Cl_2 as eluent) to yield 8.2 g (77%) as a colorless liquid. Purity: >99% (HPLC). ^{1}H-NMR ($CDCl_3$, TMS, δ, ppm): 0.87 (t, 3H, $C\underline{H}_3CH_2$-), 0.98 (d, 3H, $C\underline{H}_3CH(CH_2CH_3)$-), 1.21 and 1.42 (2m, 2H, $CH_3C\underline{H}_2$-), 1.84 (m, 1H, $CH_3CH_2C\underline{H}(CH_3)$-), 2.47 (s, 3H, -Ph-C<u>H</u>$_3$), 3.99 (d, 1H, -C<u>H</u>(Cl)-), 4.18 (m, 2H -C<u>H</u>$_2$-O-), 7.35 (d, 2ArH, m to -SO_2-), 7.79 (d, 2ArH, o to -SO_2-).

(2S, 3S)-(+)-2-Chloro-3-Methylpentyl 4'-Hydroxybiphenyl-4-carboxylate (11)

To a solution containing patassium 4'-hydroxybiphenyl-4-carboxylate (10) (6.37 g, 0.0253 mol) and 1.25 g TBAH in 100 ml dry DMSO was added compound 4 (7.00 g, 0.024 mol). The reaction mixture was stirred at 60 °C for about 20 hours, and then was poured into

300 ml H_2O. The product was extracted with chloroform. The combined chloroform extract was dried over anhydrous $MgSO_4$ and the chloroform was then removed by a rotary evaporator. The crude product was purified by precipitating from the methanol solution into water three times to remove the DMSO. The resulting solid was dried and stirred in hexane twice to remove traces amount of compound 4. The final product was then dried to yield 4.7 g (59%) of a white solid. Purity: >99% (HPLC). ^{1}H-NMR (CD_3COCD_3, TMS, δ, ppm): 0.97 (t, 3H, $C\underline{H}_3CH_2$-), 1.09 (d, 3H, $C\underline{H}_3CH(CH_2CH_3)$-), 1.36 and 1.69 (2m, 2H, $CH_3C\underline{H}_2$-), 1.98 (m, 1H, $CH_3CH_2C\underline{H}(CH_3)$-), 4.33 (d, 1H, -C<u>H</u>(Cl)-), 4.56 (m, 2H, -$COOC\underline{H}_2$-), 6.96(d, 2 ArH, o to -OH), 7.60 (d, 2 ArH, m to OH), 7.72 (d, 2 ArH, m to -COO-), 8.05 (d, 2 ArH, o to -COO-)

(2S, 3S)-(+)-2-Chloro-3-Methylpentyl 4'-(8-Vinyloxyoctyloxy)biphenyl-4-carboxylate(15-8)

Compound 11 (7.2 g, 0.0216 mol) was added to a solution of potassium carbonate (9.3 g, 0.06 mol) in 100 ml acetone. After the mixture was stirred for 2 hours at 60 °C, 8-bromooctyl-1-vinyl ether (4.83 g, 0.0206 mol) and DMSO (2 ml) were added and the reaction mixture was heated to reflux temperature overnight. Then, the reaction mixture was poured into 250 ml H_2O. The crude product was extracted several times with chloroform, and the combined chloroform extract was dried over anhydrous $MgSO_4$. After the chloroform was removed by a rotary evaporator, the remained product was stirred in 40 ml methanol with heat and cooled in an ice bath to yield a white solid, which was further purified by column chromatography (silica gel, CH_2Cl_2/C_6H_{14}=5/3 as eluent) to produce 4.0 g (40%) of monomer 15-8 as a white solid. Purity: >99.8% (HPLC). The thermal transition temperatures (°C) are: k 39.0 s_A 51.3 i on heating, and i 44.5 s_A 25.3 s_C* -18.7 k on cooling (DSC). ^{1}H-NMR ($CDCl_3$, TMS, δ, ppm): 0.94 (t, 3H, $C\underline{H}_3CH_2$-), 1.06 (d, 3H, $C\underline{H}_3CH(CH_2CH_3)$-), 1.39 (m, 8H, $=CHOCH_2CH_2(CH_2)_4$-), 1.64 (m, 4H, -$C\underline{H}_2CH_2$-OPh and $CH_3C\underline{H}_2$-), 1.80 (m, 3H, =CH-$OCH_2C\underline{H}_2$- and $CH_3CH_2C\underline{H}(CH_3)$-), 3.68 (t, 2H, =CH-$OC\underline{H}_2$-), 4.01 (m, 3H, -$C\underline{H}_2$-OPh and =$C\underline{H}_2$ trans), 4.18 (m, 1H, =$C\underline{H}_2$ cis), 4.37 (d, 1H, -C<u>H</u>(Cl)-), 4.58 (m, 2H, -$COOC\underline{H}_2$-), 6.43-6.53 (m, 1H, =C<u>H</u>-O-), 6.98(d, 2 ArH, o to -OH), 7.56 (d, 2 ArH, m to OH), 7.65 (d, 2 ArH, m to -COO-), 8.11 (d, 2 ArH, o to -COO-).

(2S, 3S)-(+)-2-Chloro-3-Methylpentyl 4'-(11-Vinyloxyundecanyloxy)biphenyl-4-carboxylate (15-11)

Monomer 15-11 was synthesized by the same procedure as the one used for the preparation of monomer 15-8. Starting from compound 11 (4.56 g, 0.0137 mol), 11-

bromoundecanyl-1-vinyl ether (4.56 g 0.0137 mol), potassium carbonate (7.0 g), 100 ml acetone and 2 ml dry DMSO we obtained 3.4 g (49%) of 15-11 as a white solid. Purity: >99.8% (HPLC). The thermal transition temperatures (°C) are: k 41.9 i on heating, and i 38.3 s_A 21.0 s_C* 0.26 k on cooling (DSC). ^{1}H-NMR ($CDCl_3$, TMS, δ, ppm): 0.96 (t, 3H, $C\underline{H}_3CH_2$-), 1.09 (d, 3H, $C\underline{H}_3CH(CH_2CH_3)$-), 1.30 (m, 8H, $=CHOCH_2CH_2(C\underline{H}_2)_4$-), 1.57 (m, 2H, $CH_3C\underline{H}_2$-), 1.69 (m, 2H, $-C\underline{H}_2CH_2$-OPh), 1.79 (m, 3H, $=CH-OCH_2C\underline{H}_2$- and $CH_3CH_2C\underline{H}(CH_3)$-), 3.67 (t, 2H, $=CH-OC\underline{H}_2$-), 4.00 (m, 3H, $-C\underline{H}_2$-OPh and $=C\underline{H}_2$ trans), 4.20 (m, 1H, $=C\underline{H}_2$ cis), 4.40 (d, 1H, $-C\underline{H}$(Cl)-), 4.60 (m, 2H, $-COOC\underline{H}_2$-), 6.42-6.53 (m, 1H, $=C\underline{H}$-O-), 6.99 (d, 2 ArH, o to -OH), 7.56 (d, 2 ArH, m to OH), 7.64 (d, 2 ArH, m to -COO-), 8.11 (d, 2 ArH, o to -COO-)

Cationic Polymerizations

Polymerizations were carried out in a three-necks round bottom flask equipped with Teflon stopcock and rubber septum under argon atmosphere at 0 °C for 1 hour. All glassware was dried overnight at 140 °C. The monomer was further dried under vacuum overnight in the polymerization flask. After the flask was filled with argon, freshly distilled dry methylene chloride was added through a syringe and the solution was cooled to 0 °C. Dimethyl sulfide and triflic acid were then added carefully via a syringe. The monomer concentration was about 0.244 M and the dimethyl sulfide concentration was 10 times larger than that of the triflic acid initiator. The polymer molecular weight was controlled by the monomer/initiator ($[M]_o/[I]_o$) ratio. After quenching the polymerization with ammoniacal methanol, the reaction mixture was precipitated into methanol. The filtered polymers were purified by precipitating from methylene chloride solution into methanol. The resulted polymers were dried in a vacuum oven.

RESULT AND DISCUSSION

Liquid crystalline polymers exhibiting chiral mesophases are of both theoretical and technological interest[21,24,25]. Although some empirical rules are available for the synthesis of low-molar-mass liquid crystals displaying a chiral smectic C (s_C*) mesophase[26], they are not yet available for the design of side chain liquid crystalline polymers[9-21,24,25]. Therefore, we have been concentrating on developing such empirical rules useful for the molecular engineering of side chain liquid crystalline polymers exhibiting a s_C* mesophase.

The synthesis of monomers 15-11 and 15-8 is outlined in Scheme I. The synthetic method used for the synthesis of compound 2 from compound 1 is well established[10,23] and

t 'es place with the retention of configuration of L-isoleucine. L-alanine[23a], D-alanine[23a], L-leucine[10] and L-Isoleucine[23b,c] were converted to L-chloropropionic acid, D-chloropropionic acid, S-(+)-2-chloro-4-methylpentanoic acid and (2S, 3S)-(+)-2-chloro-3-methylpentanoic acid, respectively, without detectable racemization. Therefore, the resulted compound 2 and the subsequent monomers 15-11 and 15-8 should maintain the same configuration as L-isoleucine. The cationic polymerization of 15-11 and 15-8 was initiated with $CF_3SO_3H/S(CH_3)_2$ system[27] at 0 °C in CH_2Cl_2. The polymerization mechanism is presented in Scheme II. The polymerization results are summarized in Tables I and II. As we can see from both Tables I and II, polymer yields are lower than expected. This is due to the polymer loss during the purification process. Absolute number average molecular weights are difficult to be determined by ^{1}H-NMR spectroscopy because of the signals overlap. Relative molecular weights determined by GPC using polystyrene as a calibration standard demonstrate that the ratio of $[M]_o/[I]_o$ provides a very good control of the polymer molecular weight. In addition, all polydispersities are lower than 1.15. The relative relationships of number average molecular weights and polydispersities determined by GPC versus $[M]_o/[I]_o$ for both poly(15-11)s and poly(15-8)s are plotted in Figure 1. Within experimental errors all these dependences are close to linear.

Mesomorphic behaviors of both poly(15-11)s and poly(15-8)s were determined by DSC and thermal optical polarized microscopy. Figure 2 presents the DSC traces of poly(15-11)s with various degrees of polymerization. The DSC curves of the second scans (Fig. 2(b)) are different from those of the first heating scans (Fig. 2(a)), but similar to those of the subsequent heating scans. The DSC curves of the first cooling scans are similar to those of the subsequent cooling scans. Phase transition temperatures and corresponding enthalpy changes are summarized in Table I. The dependence of mesomorphic transition temperatures on the degree of polymerization of poly(15-11)s is plotted in Figure 3. It is clear from Figure 3 that all poly(15-11)s with various degree of polymerization are crystalline and above the melting temperature exhibit enantiotropic S_C^* and S_A mesophases. These mesophases are confirmed by thermal optical polarized microscopy. The representative textures of S_C^* and S_A mesophases are presented in Figure 4. Since crystallization is a kinetically controlled process and the formation of a mesophase is a thermodynamically controlled process, the crystalline peaks are different in the first and second heating scans while mesomorphic transition temperatures remain the same. The plots from Figure 3 indicate the strong influence of molecular weight on phase transition temperatures.

The DSC traces of first and second heating and first cooling scans of poly(15-8)s with various molecular weights are presented in Figure 5. Mesomorphic transition temperatures and corresponding enthalpy changes are summerized in Table II. The dependence of various mesomorphic transition temperatures on the molecular weight of poly(15-8)s are plotted in Figure 6. As we can observe from Figures 5 and 6, poly(15-8)s show enantiotropic s_C^* and s_A mesophases over the entire range of molecular weights. The transition temperatures of s_C^* to s_A of poly(15-8)s with degrees of polymerization up to 6 are overlapped with the broad transition peak of the s_A to isotropic phase transition. In addition, poly(15-8)s with degrees of polymerization higher than 12 exhibit an unidentified enantiotropic smectic (s_X) mesophase. Due to the thermodynamically controlled nature of these mesomorphic transitions, the DSC traces from first and second heating scans are similar.

Let us compare the mesomorphic behavior of poly(15-11)s and poly(15-8)s. Both poly(15-11)s and poly(15-8)s exhibit enantiotropic s_C^* and s_A mesophases. The transition temperatures of poly(15-8)s from s_C^* to s_A are about 25-30 °C higher than those of poly(15-11)s, while the transition temperatures of poly(15-8)s from s_A to isotropic phase are about 5 to 10 °C lower than those of poly(15-11)s. Therefore, the s_C^* mesophase of poly(15-8)s is more stable and appears over a broader temperature range. In addition, poly(15-8)s with degrees of polymerization higher than 12 exhibit an additional s_X mesophase. On the other hand, all poly(15-11)s undergo side chain crystallization, while poly(15-8)s does not crystallize at all.

The copolymerization of 15-11 with 15-8 is outlined in Scheme III and the copolymerization results are summerized in Table III. All copolymerizations lead to almost quantitative conversions (determined by TLC). The copolymerization yields are lower than quantitative due to the polymer loss during the purification process. Therefore, the copolymer composition is identical to the monomer feed[6,7,22c]. Attempts were made to synthesize poly(15-11-co-15-8)X/Y (where X/Y refers to the mole ratio of the two structure units) with the degree of polymerization of about 15. We can observe from Table III that the relative number average molecular weight of copolymers are very well controlled by the $[M]_0/[I]_0$ ratio and the polydispersities of all copolymers are lower than 1.11. Figure 7 presents the DSC traces of poly(15-11-co-15-8)X/Y obtained during first and second heating and first cooling scans. The mesomorphic behavior of poly(15-11-co-15-8)X/Y as a function of copolymer composition can be observed from Figure 8. It is clear that all poly(15-11-co-15-8)X/Y with X/Y=1/9-9/1 exhibit enantiotropic s_C^* and s_A mesophases. According to the dependences from Figure 8 the structural units of poly(15-11)s and poly(15-8)s are isomorphic in their s_A and s_C^* mesophases but not in their s_X mesophase of poly(15-8)s and in the crystalline phase

of poly(15-11)s. Therefore, copolymerization of 15-11 and 15-8 supresses the s_X mesophase resulted from poly(15-8)s and the crystalline phase due to poly(15-11)s. Consequently poly(15-11-co-15-8)X/Y with X/Y=1/9-4/6 are noncrystallizable copolymers exhibiting an enantiotropic s_C* mesophase over a broad range of temperature, i.e., from 15 °C to 65-90 °C.

The results of these copolymerization experiments have demonstrated how living cationic polymerization can be used to engineer the transition temperature of a s_C* mesophase.

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REFERENCES

1. a) J. M. Rodriguez-Parada and V. Percec, *J. Polym. Sci., Part A: Polym. Chem.*, 1986, **29**, 327; b) V. Percec and D. Tomazos, *Polym. Bull.*, 1987, **18**, 239; c) V. Percec, *Makromol. Chem., Macromol. Symp.*, 1988, **13/14**, 397.
2. a) T. Sagane and R. W. Lenz, *Polym. J.*, 1988, **20**, 923; b) T. Sagane and R. W. Lenz, *Polymer*, 1989, **30**, 2269; c) T. Sagane and R. W. Lenz, *Macromolecules*, 1989, **22**, 3763.
3. S. G. Kostromin, N. D. Cuong, E. S. Garina and V. P. Shibaev, *Mol. Cryst. Liq. Cryst.*, 1990, **193**, 177.
4. a) V. Heroguez, A. Deffieux and M. Fontanille, *Makromol. Chem., Macromol. Symp.*, 1990, **32**, 199; b) V. Heroguez, M. Schappacher, E. Papon and A. Deffieux, *Polym. Bull.*, 1991, **25**, 307.
5. a) V. Percec, M. Lee and H. Jonsson, *J. Polym. Sci.: Part A: Polym. Chem.*, 1991, **29**, 327; b) V. Percec and M. Lee, *Macromolecules*, 1991, **24**, 1017; c) V. Percec and M. Lee, *Macromolecules*, 1991, **24**, 2780; d) V. Percec, M. Lee and C. Ackerman, *Polymer*, in press; e) V. Percec and M. Lee, *J. Macromol. Sci.-Chem.*, 1991, **A28** 651.
6. a) V. Percec, A. Gomes and M. Lee, *J. Polym. Sci.: Part A: Polym. Chem.*, 1991, **29**,1615; b) H. Jonsson, V. Percec and A. Hult, *Polym. Bull.*, 1991, **25**, 115; c) R. Rodenhouse and V. Percec, *Adv. Mater.*, 1991, **3**, 101; d) R. Rodenhouse and V. Percec, *Polym. Bull.* 1991, **25**, 47; e) R. Rodenhouse, V. Percec and A. E. Feiring, *J. Polym. Sci: Part C: Polym. Lett.*, 1990, **28**, 345; f) V. Percec, C. S. Wang and M. Lee, *Polym. Bull.*, 1991, **26**, 15.

7. a) V. Percec and M. Lee., *Polymer*, in press; b) V. Percec and M. Lee, *Polym. Bull.*, 1991, **25**, 123; c) V. Percec and M. Lee, *Polym. Bull.*, 1991, **25**, 131; d) V. Percec and M. Lee, *Macromolecules*, 1991, **24**, 4963; e) V. Percec and M. Lee, *J. Mater. Chem.*, in press.

8. a) R. B. Meyer, L. Libert, L. Strzelecki and P. Keller, J. Phys., 1975, **36**, L-69; b) R. B. Meyer, *Mol. Cryst. Liq. Cryst.*, 1977, **40**, 33.

9. V. P. Shibaev, M. V. Kozlovsky, L. A. Beresnev, L. M. Blinov and N. A. Plate, *Polym. Bull.* 1984, **12**, 299.

10. V. P. Shibaev, M. V. Kozlovsky, N. A. Plate L. A. Beresnev and L. M. Blinov, *Polym. Sci. USSR*, 1987, **29**, 1616.

11. a) G. Decobert, F. Soyer and J. C. Dubois, *Polym. Bull.* 1985, **14**, 179; b) J. M. Guglielminetti, G. Decobert and J. C. Dubois, *Polym. Bull.* 1986, **16**, 411; c) J. C. Dubois, G. Decobert, P. LeBarny, S. Esselin, C. Friedrich and C. Noel, *Mol. Cryst. Liq. Cryst.* 1986, **137**, 349; d) G. Decobert, J. C. Dubois, S. Esselin and C. Noel, *Liq. Cryst.*, 1986, **1**, 307; e) S. Esselin, L. Bosios, C. Noel, G. Decobert and J. C. Dubois, *Liq. Cryst.* 1987, **2**, 505; f) S. Esselin, C. Noel, G. Decobert and J. C. Dubois, *Mol. Cryst. Liq. Cryst.*, 1988, **155**, 371.

12. a) R. Zentel, G. Reckert and B. Reck, *Liq. Cryst.*, 1987, **2**, 83; b) S. Bualek and R. Zentel, *Makromol. Chem.*, 1988, **189**, 797; c) H. Kapitza and R. Zentel, *Makromol. Chem.*, 1988, **189**, 1793; d) S. Bualek, H. Kapitza, J. Meyer, G. F. Schmidt and R. Zentel, *Mol. Cryst. Liq. Cryst.*, 1988, **155**, 47; e) S. U. Vallerien, R. Zentel, F. Kremer, H. Kapitza and E. W. Fischer, *Makromol. Chem. Rapid Commun.* 1989, **10**, 333; f) R. Zentel, H. Kapitza, F Kremer and S. U. Vallerien, in "*Liquid Crystalline Polymers*", R. A. Weiss and C. K. Ober Eds., ACS Symposium Series 435, Washington DC., 1990, p. 207.

13. a) S. Uchida, K. Morita, K. Miyoshi, K. Hashimoto and K. Kawasaki, *Mol. Cryst. Liq. Cryst.*, 1988, **155**, 93; b) H. Endo, S. Hachiya, S. Uchida, K. Hashimoto and K. Kawasaki, *Liq. Cryst.*, 1991, **9**, 635.

14. N. Koide, K. Uehara and K. Iimura, *Mol. Cryst. Liq. Cryst.*, 1988, **157**, 151.

15. T. Suzuki, T. Okawa, K. Ohnuma and Y. Sakon, *Makromol. Chem. Rapid Commun.*, 1988, **9**, 755.

16. M. Dumon, H. T. Nguyen, M. Mauzac, C. Destrade, M. F. Achard and H. Gasparoux, *Macromolecules*, 1990, **23**, 355.

17. D. M. Walba, P. Keller, D. S. Parmar, N. A. Clark and M. D. Wand, *J. Am. Chem. Soc.* 1989, **111**, 8273.

18. H. Kapitza, R. Zentel, R. J. Twieg, C. Nguyen, S. U. Vallerien, F. Kremer and C. G. Willson, *Adv. Mater.* 1990, **2**, 539.

19. T. Kitazume, T. Ohnogi and K. Ito, *J. Am. Chem. Soc.* 1990, **112**, 6608.

20. a) H. J. Cole, H. F. Gleeson, G. Scherowsky and A. Schliwa, *Mol. Cryst. Liq. Cryst.*, 1990, **7**, 117 and 125; b) H. M. Colquhoun, C. C. Dudman, C. A. O'Makoney, G. C. Robinson and D. J. Williams, *Adv. Mater.*, 1990, **2**, 139; c) J. Naciri, S. Pfeiffer and R. Shashidhar, *Liq. Cryst.*, 1991, **10**, 585.

21. P. LeBarny and J. C. Dubois, in "*Side Chain Liquid Crystal Polymers*", C. B. McArdle Ed., Chapman and Hall, New York, 1989, p. 130.

22. a) V. Percec, Q. Zheng and M. Lee, J Mater. Chem., 1991, 1, 611; b) V. Percec, Q. Zheng and M. Lee, J Mater. Chem., in press; c) V. Percec and C. S. Wang, *J. Macromol. Sci.-Chem.*, 1991, **A28**, 687; d) V. Percec and C. S. Wang, *J. Macromol. Sci.-Chem.*, 1991, **99**, A-29; e) V. Percec, C. S. Wang, and M. Lee, *Polym. Bull.*, 1991, **26**, 15.

23. a) S. J. Fu, S. M. Birnbaum and J. P. Greentein, *J. Am. Chem. Soc.*, 1954, **76**, 6056; b) K. Yoshino, N. Mikami, R. Higuchi and M. Honma, *Mol. Cryst. Liq. Cryst.*, 1987, **144**, 18; c) M. Dumon, H. T. Nguyen, M. Mauzac, C. Destrade and H. Gasparoux, *Liq. Cryst.*, 1991, **10**, 475.

24. V. P. Shibaev and Ya. S. Freidzon, in "*Side Chain Liquid Crystal Polymers*", C. B. McArdle Ed., Chapman and Hall, New York, 1989, p. 260.

25. J. H. Wendorff, *Angew. Chem., Int. Ed., Engl.*, 1991, **30**, 405, and references cited therein.

26. a) G. W. Gray and J. W. Goodby, *Mol. Cryst. Liq. Cryst.*, 1976, **37**, 157; b) G. W. Gray and J. W. Goodby, *Mol. Cryst. Liq. Cryst.*, 1978, **48**, 127; c) G. W. Gray, M. Hird, D. Lacey and K. J. Toyne, *Mol. Cryst. Liq. Cryst.*, 1990, **191**, 1; d) D. Demus, H. Demus and H. Zaschke, *Flussige Kristalle in Tabellen*, I and II, VEB Deutscher Verlag fur Grundstoffindustrie, Leipzig, 1974 and 1984; e) D. M. Walba, C. S. Slater, W. N. Thurmes, N. A. Clark, M. A. Handsky and F. Supon, *J. Am. Chem. Soc.*, 1986, **108**, 5210.

27. a) C. G. Cho, B. A. Feit and O. W. Webster, *Macromolecules*, 1990, **23**, 1918; b) C. H. Lin and K. Matyjaszewsky, *Polym. Prepr., Am. Chem. Soc. Div. Polym. Chem.*, 1990, **31(1)**, 599.

FIGURES AND SCHEME CAPTIONS

Scheme I: Synthesis of (2S, 3S)-(+)-2-chloro-3-methylpentyl 4'-(11-vinyloxyundecanyloxy) biphenyl-4-carboxylate (15-11) and (2S, 3S)-(+)-2-chloro-3-methylpentyl 4'-(8-vinyloxyoctyloxy)biphenyl-4-carboxylate (15-8).

Scheme II: Cationic polymerization of (2S, 3S)-(+)-2-chloro-3-methylpentyl 4'-(11-vinyloxyundecanyloxy)biphenyl-4-carboxylate (15-11) and (2S, 3S)-(+)-2-chloro-3-methylpentyl 4'-(8-vinyloxyoctyloxy)biphenyl-4-carboxylate (15-8).

Scheme III: Cationic copolymerization of (2S, 3S)-(+)-2-chloro-3-methylpentyl 4'-(11-vinyloxyundecanyloxy)biphenyl-4-carboxylate (15-11) and (2S, 3S)-(+)-2-chloro-3-methylpentyl 4'-(8-vinyloxyoctyloxy)biphenyl-4-carboxylate (15-8).

Figure 1: The dependence of the number average molecular weight (Mn) ■ and polydispersity (Mw/Mn) ▲ determined by GPC on the $[M]_o/[I]_o$ ratio. (a) data from poly(15-11)s; (b) data from poly(15-8)s.

Figure 2: DSC traces of poly(15-11)s with different degrees of polymerization (DP) determined by GPC. DP is printed on the top of each DSC scan. (a) first heating scan; (b) second heating scan; (c) first cooling scan.

Figure 3: The dependence of phase transition temperatures on the degree of polymerization determined by GPC of poly(15-11)s. (a) data from the first heating scan: ◘ -T(k-s_C*) △ -T(s_C*-s_A) □ -T(s_A-i); b) data from the second heating scan: ◘ -T(k-s_C*) △ -T(s_C*-s_A) □ -T(s_A-i); c) data from the first cooling scan: ■ -T(i-s_A) ▲ -T(s_A-s_C*) ■ -T(s_C*-k).

Figure 4: Representative optical polarized micrographs (100x) of: (a) the s_A mesophase displayed by poly(15-11) (DP=13) at 87.3 °C on the cooling scan ; (b) the s_C* mesophase displayed by poly(15-11) (DP=13) at 30.0 °C on the cooling scan.

Figure 5: DSC traces of poly(15-8)s with different degrees of polymerization (DP) determined by GPC. DP is printed on the top of each DSC scan. (a) first heating scan; (b) second heating scan; (c) first cooling scan.

Figure 6: The dependence of phase transition temperatures on the degree of polymerization determined by GPC of poly(15-8)s. (a) data from the first heating scan: ○ -T(g-s_C*); ○ -T(g-s_X); ▫ -T(s_X-s_C*); △ -T(s_C*-s_A) □ -T(s_A-i); (b) data from the second heating scan: ○ -T(g-s_C*); ○ -T(g-s_X); ▫ -T(s_X-s_C*); △ -T(s_C*-s_A) □ -T(s_A-i); (c) data from the first cooling scan: ■ -T(i-s_A); ▲ -T(s_A-s_C*); ▪ -T(s_C*-s_X); ● -T(s_C*-g); ● -T(s_X-g).

Figure 7: DSC traces of poly(15-11-co-15-8)X/Y with different degrees of polymerization (DP) determined by GPC.Copolymer composition is printed on the top of each DSC scan. (a) first heating scan; (b) second heating scan; (c) first cooling scan.

Figure 8: The dependence of phase transition temperatures on copolymer composition of poly(15-11-co-15-8)X/Y. (a) data from the first heating: ○ -T(g-s_C*); ○ -T(g-s_X); ◇ -T(s_X-s_C*); ▫ -T(k-s_C*); △ -T(s_C*-s_A) □ -T(s_A-i); (b) data from the second heating scan: ○ -T(g-s_C*); ○ -T(g-s_X); ◇ -T(s_X-s_C*); ▫ -T(k-s_C*); △ -T(s_C*-s_A) □ -T(s_A-i); (c) data from the first cooling scan: ■ -T(i-s_A); ▲ -T(s_A-s_C*); ◆ -T(s_C*-s_X); ● -T(s_C*-g); ▫ -T(s_C*-k).

Table I. Cationic polymerization of (2S,3S)-(+)-2-chloro-3-methylpentyl 4'-(11-vinyloxyundecanoxy)biphenyl-4-carboxylate (15-11) (polymerization temperature: 0 °C; polymerization solvent: methylene chloride; $[M]_o$=0.244; $[(CH_3)_2S]_o/[I]_o$ =10; polymerization time: 1hr) and characterization of the resulting polymers. Data on first line under heating are from first heating scan. Data on second line under heating are from second heating scan.

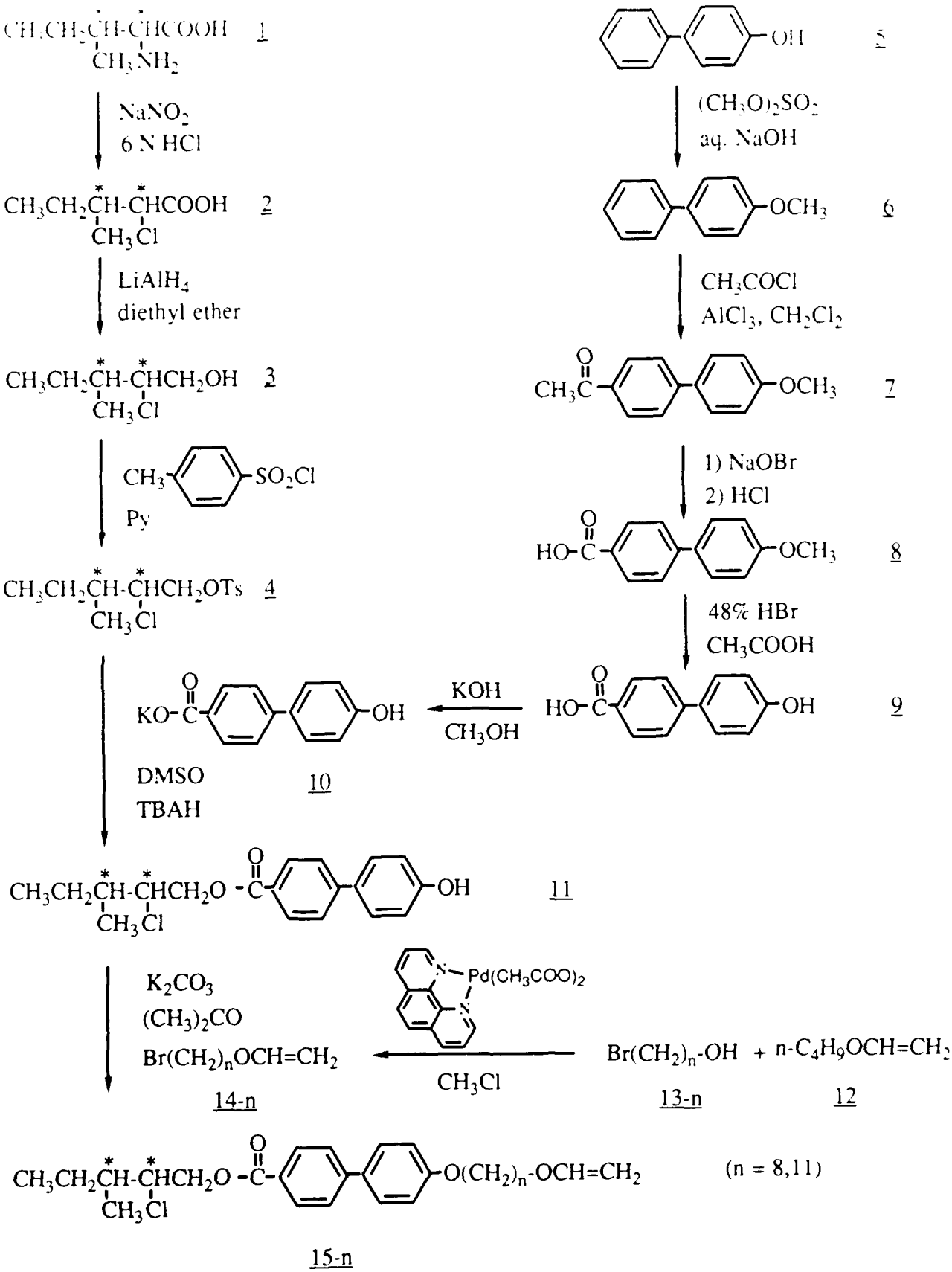
Sample No.	$[M]_o/[I]_o$	Polymer yield(%)	Mnx 10^{-3}	Mw/Mn G P C	D P	phase transitions (°C) and corresponding enthalpy changes (kcal/mru) heating	cooling
1	3	63	2.06	1.07	4	k 39.0 (0.788) s_C* 52.3 (0.0265) s_A 80.5 (1.34) i	i 71.0 (-1.36) s_A 44.1 (-0.0423) s_C* 0.07 (-0.900) k
						k 19.1 (0.857) s_C* 52.1 (0.0370) s_A 80.6 (1.35) i	
2	4	61	2.69	1.09	5	k 46.0 (2.38) s_C* 53.3 (0.047) s_A 85.4 (1.46) i	i 77.9 (-1.30) s_A 48.0 (0.048) s_C* 3.14 (-0.651) k
						k 17.6 (0.73) s_C* 53.7 (0.058) s_A 84.6 (1.56) i	
3	8	60	4.49	1.16	8	k 43.2 (2.25) s_C* 55.3 (0.053) s_A 98.2 (1.26) i	i 92.08 (-1.19) s_A 50.8 (-0.053) s_C* 12.7 (-0.73) k
						k 23.1 (0.71) s_C* 54.9 (0.032) s_A 98.0 (1.25) i	
4	12	86	6.86	1.10	13	k 52.1 (1.13) s_C* 59.0 (0.038) s_A 109.3 (1.17) i	i 101.6 (-1.14) s_A 54.1 (-0.026) s_C* 21.1 (-0.86) k
						k 33.5 (1.14) s_C* 59.3 (0.026) s_A 108.7 (1.13) i	
5	16	89	8.11	1.08	15	k 47.7 (2.68) s_C* 59.1 (0.011) s_A 109.3 (1.13) i	i 101.4 (-1.29) s_A 54.2 (-0.023) s_C* 22.8 (-0.97) k
						k 34.4 (1.08) s_C* 58.8 (0.016) s_A 108.2 (1.06) i	
6	20	76	8.26	1.07	16	k 47.8 (2.78) s_C* 59.9 (0.039) s_A 111.4 (1.25) i	i 104.1 (-1.22) s_A 55.1 (-0.042) s_C* 23.0 (-1.00) k
						k 35.0 (0.89) s_C* 60.2 (0.042) s_A 110.8 (1.25) i	
7	25	93	11.2	1.15	21	k 47.7 (1.98) s_C* 60.9 (0.010) s_A 114.3 (1.06) i	i 107.0 (-1.02) s_A 56.0 (-0.026) s_C* 27.6 (-0.87) k
						k 39.5 (1.02) s_C* 60.6 (0.021) s_A 114.0 (1.03) i	

Table II. Cationic polymerization of (2S,3S)-(+)-2-chloro-3-methylpentyl 4'-(8-vinyloxyoctoxy)biphenyl-4-carboxylate (15-8) (polymerization temperature: 0 °C; polymerization solvent: methylene chloride; $[M]_0$=0.244; $[(CH_3)_2S]_0/[I]_0$=20; polymerization time: 1hr) and characterization of the resulting polymers. Data on first line under heating are from first heating. Data on second line under heating are from second heating scan.

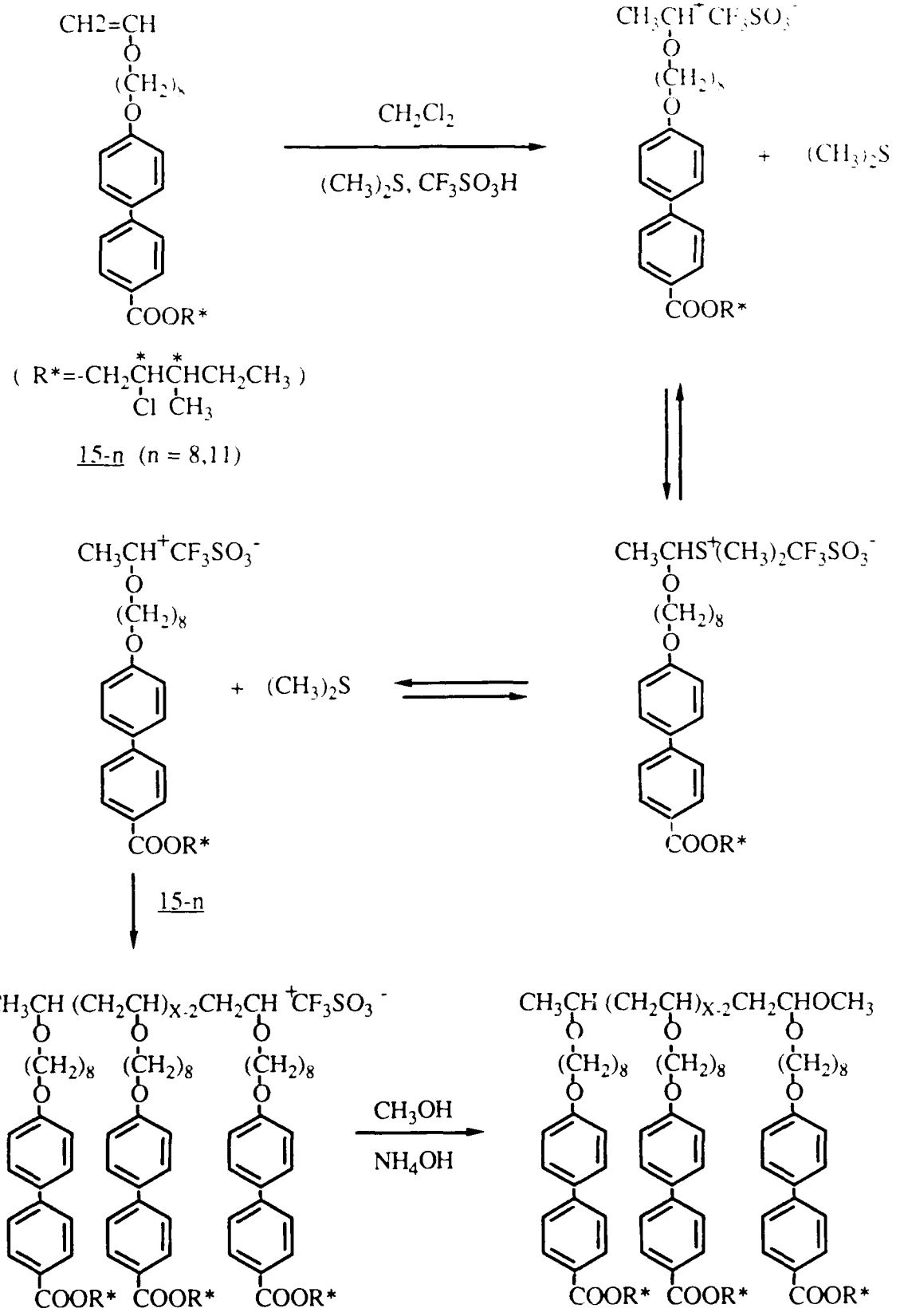
Sample No.	$[M]_0/[I]_0$	Polymer yield(%)	$Mn \times 10^{-3}$ GPC	Mw/Mn GPC	DP	phase transitions (°C) and corresponding enthalpy changes (kcal/mru) heating	cooling
1	3	55	2.00	1.08	4	g -2.7 s_C^* 77.9 (1.27) i	i 69.2 (1.24) s_C^* -9.4 g
						g -3.0 s_C^* 77.8 (1.28) i	
2	4	58	2.70	1.11	6	g 5.0 s_C^* 84.9 (1.18) i	i 76.2 (1.13) s_C^* -3.0 g
						g 4.5 s_C^* 85.2 (1.15) i	
3	5	41	3.42	1.14	7	g 5.54 s_C^* 81.8 (0.122) s_A 88.9 (0.896) i	i 81.4 (-1.85) s_A 76.4 (-0.146) s_C^* -1.84 g
						g 3.91 s_C^* 81.6 (0.122) s_A 88.8 (0.901) i	
4	8	47	3.81	1.08	8	g 6.30 s_C^* 83.5 (0.122) s_A 91.5 (1.02) i	i 84.81 (-0.945) s_A 78.9 (0.127) s_C^* -0.08 g
						g 4.83 s_C^* 83.0 (0.117 s_A 91.1 (0.886) i	
5	12	58	5.45	1.09	11	g 6.31 s_C^* 81.4 (0.175) s_A 91.2 (0.906) i	i 84.9 (-0.818) s_A 79.1 (-0.146) s_C^* 2.23 g
						g 5.86 s_C^* 84.0 (0.175) s_A 92.3 (0.867) i	
6	16	66	6.08	1.07	12	g 12.6 s_X 37.4 (0.0779) s_C^* 89.9 (0.166) s_A 99.2 (0.974) i	i 89.9 (-0.828) s_A 84.1 (-0.107) s_C^* 29.79 (-0.0730) s_X 8.92 g
						g 12.3 s_X 36.3 (0.0633) s_C^* 89.2 (0.166) s_A 98.0 (0.886) i	
7	20	65	6.17	1.08	13	g 15.2 s_X 43.0 (0.039) s_C^* 92.0 (0.141) s_A 101.8 (1.04) i	i 92.6 (-0.862) s_A 86.9 (-0.156) s_C^* 35.6 (-0.458) s_X 10.3 g
						g 15.0 s_X 41.6 (0.0548) s_C^* 90.9 (0.170) s_A 100.0 (0.891) i	
8	25	77	8.59	1.08	18	g 21.7 s_X 53.1 (0.127) s_C^* 94.1 (0.166) s_A 104.1 (0.823) i	i 94.3 (-0.772) s_A 86.9 (-0.144) s_C^* 46.5 (-0.117) s_X 15.2 g
						g 18.2 s_X 52.7 (0.132) s_C^* 93.6 (0.146) s_A 103.8 (0.809) i	

Table III Cationic copolymerization of (15-11) with (15-8) (polymerization temperature: 0 °C; polymerization solvent: methylene chloride; $[M]_0=[15\text{-}11]+[15\text{-}8]=0.208$-$0.244$M; $[M]_0/[I]_0=15$; $[(CH_3)_2S]_0/[I]_0=10$; polymerization time: 1hr) and characterization of the resulting polymers. Data on first line under heating are from first heating. Data on second line under heating are from second heating scan.

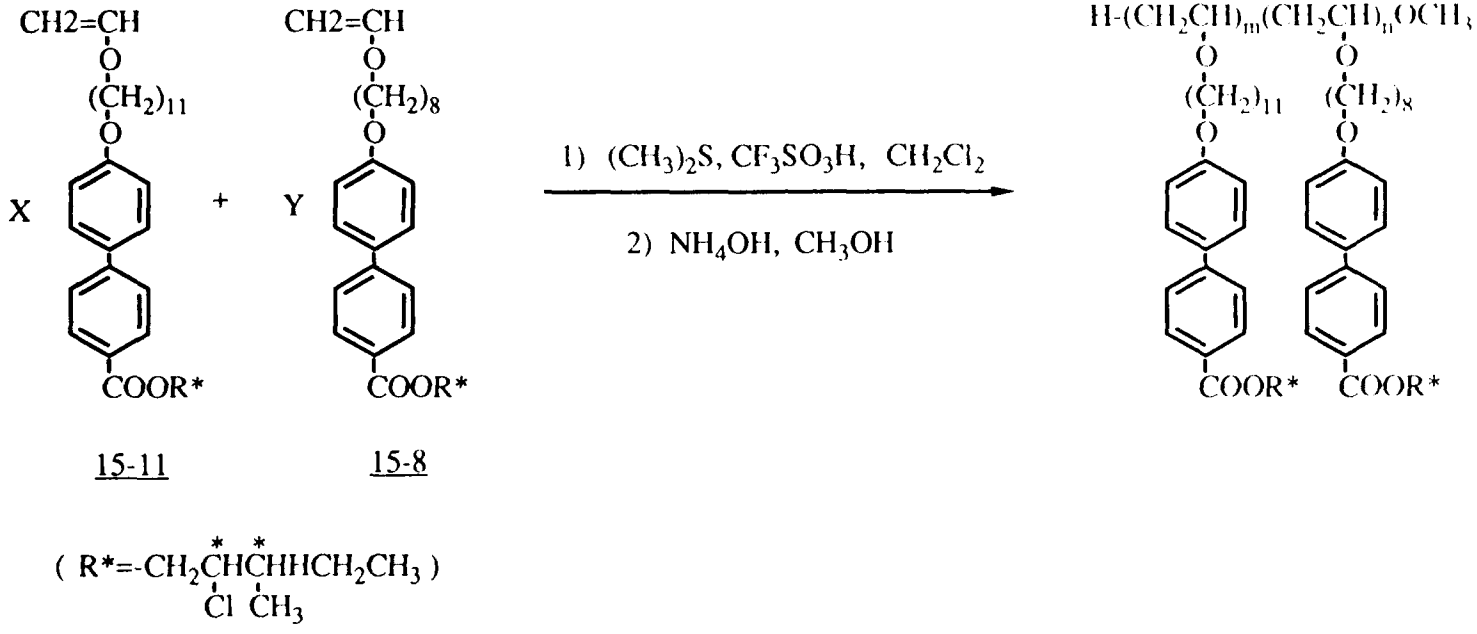
Sample No.	[15-11]/[15-8] (mol/mol)	Polymer yield(%)	Mnx10^{-3}	Mw/Mn GPC	D.P.	phase transitions (°C) and corresponding enthalpy changes (kcal/mru)	
						heating	cooling
1	0/10	66	6.08	1.07	12	g 12.6 s_X 37.4 (0.0779) s_C* 89.9 (0.166) s_A 99.2 (0.974) i g 12.3 s_X 36.3 (0.0633) s_C* 89.2 (0.166) s_A 98.0 (0.886) i	i 89.9 (-0.828) s_A 84.1 (-0.107) s_C* 29.79 (-0.0730) s_X 8.92 g
2	1/9	85	7.16	1.06	15	g 14.2 s_C* 90.0 (0.0983) s_A 104.5 (0.973) i g 13.0 s_C* 89.6 (0.123) s_A 104.1 (0.988) i	i 94.3 (-0.929) s_A 83.3 (-0.103) s_C* 12.0 g
3	2/8	83	6.50	1.07	13	g 10.0 s_C* 82.5 (0.114) s_A 102.5 (1.03) i g 9.5 s_C* 81.7 (0.109) s_A 101.7 (1.04) i	i 92.8 (-0.976) s_A 75,3 (-0.0842) s_C* 8.0 g
4	3/7	79	5.78	1.11	12	g 10.2 s_C* 71.4 (0.0800) s_A 98.7 (1.04) i g 9.00 s_C* 71.6 (0.0590) s_A 98.8 (1.04) i	i 89.5 (-1.01) s_A 65.3 (-0.0800) s_C* 2.0 g
5	4/6	80	5.93	1.10	12	g 10.2 s_C* 64.7 (0.0534) s_A 99.8 (1.09) i g 10.0 s_C* 64.8 (0.0534) s_A 99.8 (1.11) i	i 90.9 (-1.06) s_A 59.2 (-0.0550) s_C* 2.76 g
6	5/5	75	6.61	1.06	13	k 20.1 (0.0915) s_C* 61.9 (0.0350) s_A 102.8 (1.07) i k 19.4 (0.102) s_C* 61.7 (0.0305) s_A 102.7 (1.08) i	i 94.3 (-1.05) s_A 55.5 (-0.0457) s_C* 10.2 (-0.0965) k
7	6/4	81	6.86	1.06	13	k 21.7 (1.12) s_C* 57.3 (0.0359) s_A 104.6 (1.08) i k 21.7 (0.179) s_C* 57.3 (0.0539) s_A 104.6 (1.09) i	i 95.11 (-1.04) s_A 50.4 (-0.0461) s_C* 11.2 (-0.310) k
8	7/3	75	6.72	1.06	13	k 45.8 (0.878) s_C* 54.9 (0.0207) s_A 105.7 (0.940) i k 22.8 (0.212) s_C* 54.7 (0.0207) s_A 105.1 (0.919) i	i 97.2 (-0.878) s_A 48.6 (-0.0207) s_C*13.1 (0.258) k
9	8/2	80	7.63	1.07	15	k 46.4 (1.64) s_C* 56.4 (0.0312) s_A 108.1 (1.12) i k 27.0 (0.474) s_C* 55.5 (0.0312 s_A 108.1 (1.14) i	i 99.5 (-1.11) s_A 48.3 (-0.0260) s_C* 15.9 (-0.401) k
10	9/1	72	7.18	1.06	14	k 54.1 (2.38) s_A 108.2 (1.10) i k 29.7 (0.693) s_C* 59.3 (0.0315) s_A 107.9 (1.11) i	i 99.4 (-1.08) s_A 52.77 (-0.0360) s_C* 18. (-0.588) k
11	10/0	77	6.86	1.10	13	k 52.1 (1.13) s_A 109.3 (1.17) i k 33.5 (1.14) s_C* 59.3 (0.0260) s_A 108.7 (1.13) i	i 101.6 (-1.14) s_A 54.1 (-0.0260) s_C* 21.1 (-0.860) k


CH3CH2CH-CHCOOH 1
CH3 NH2
NaNO2
6 N HCl
CH3CH2CH-CHCOOH 2
CH3 Cl
LiAlH4
diethyl ether
CH3CH2CH-CHCH2OH 3
CH3 Cl
CH3 SO2Cl
Py
CH3CH2CH-CHCH2OTs 4
CH3 Cl
OH 5
(CH3O)2SO2
aq. NaOH
OCH3 6
CH3COCl
AlCl3, CH2Cl2
CH3C O OCH3 7
1) NaOBr
2) HCl
HO-C O OCH3 8
48% HBr
CH3COOH
HO-C O OH 9
KO-C O OH 10
KOH
CH3OH
DMSO
TBAH
CH3CH2CH-CHCH2O-C O OH 11
CH3 Cl
K2CO3
(CH3)2CO
Br(CH2)nOCH=CH2
14-n
Pd(CH3COO)2
CH3Cl
Br(CH2)n-OH + n-C4H9OCH=CH2
13-n 12
CH3CH2CH-CHCH2O-C O O(CH2)n-OCH=CH2 (n = 8,11)
CH3 Cl
15-n

Scheme I


CH2=CH
(CH2)x
COOR*
CH2Cl2
(CH3)2S, CF3SO3H
CH3CH+CF3SO3-
(CH3)2S
(R*=-CH2CHCHCH2CH3)
Cl CH3
15-n (n = 8,11)
CH3CH+CF3SO3-
(CH3)8
+ (CH3)2S
CH3CHS+(CH3)2CF3SO3-
15-n
CH3CH (CH2CH)X-2CH2CH +CF3SO3 -
CH3OH
NH4OH
CH3CH (CH2CH)X-2CH2CHOCH3

Scheme II



15-11 15-8

(R*=-$CH_2\overset{*}{C}H\overset{*}{C}HHCH_2CH_3$)
Cl CH_3

Scheme III

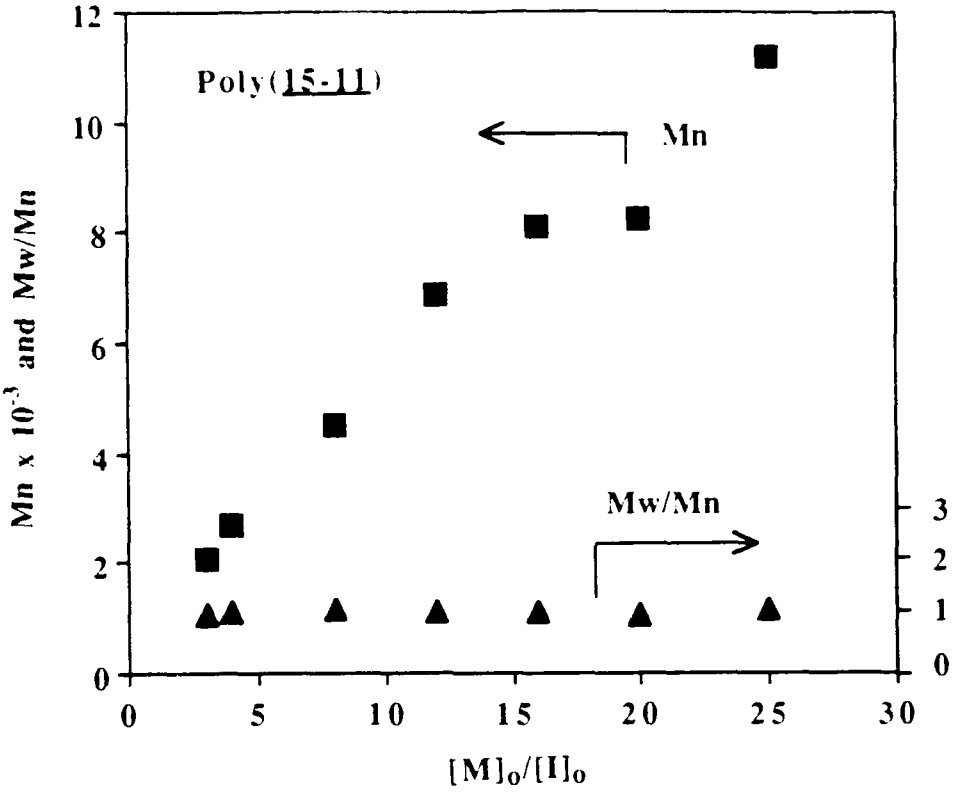


Figure 1. (a)

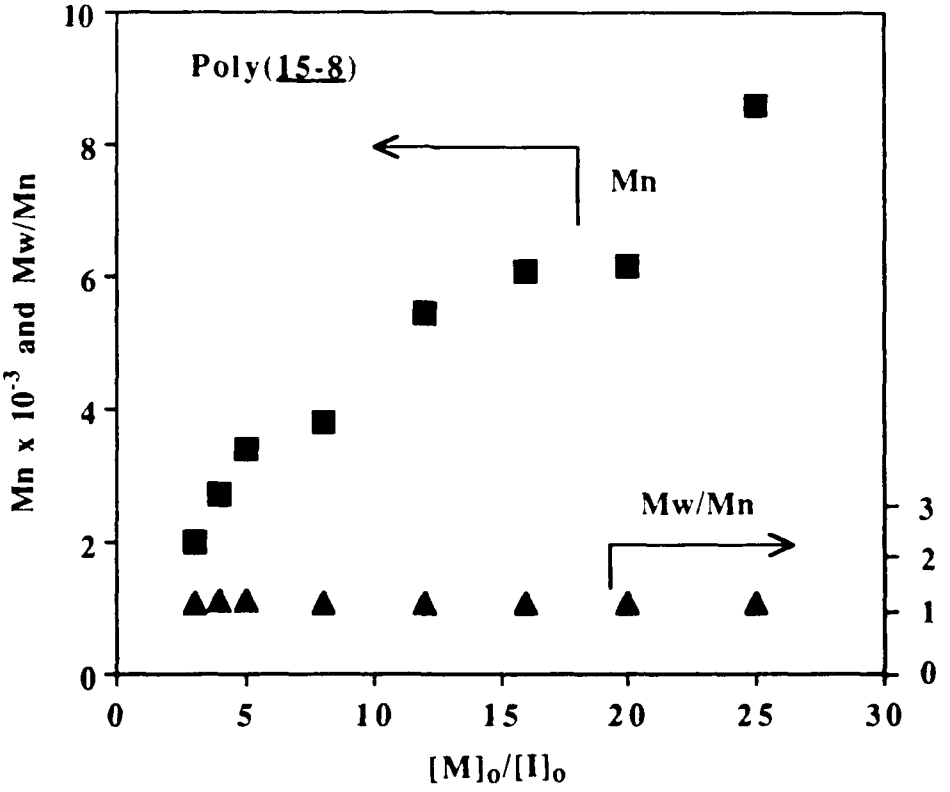


Figure 1. (b)

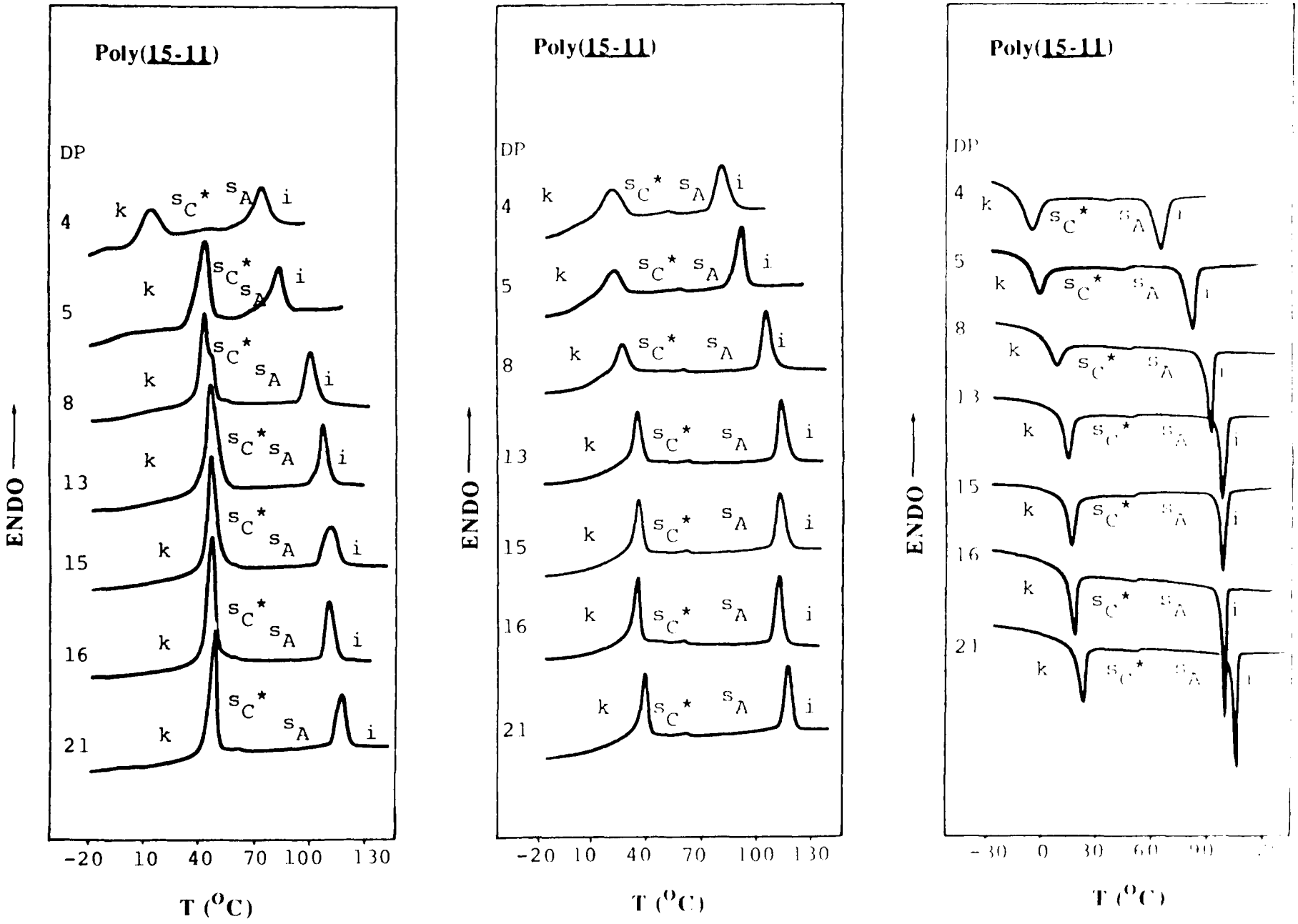

Poly(15-11)
DP
4
5
8
13
15
16
21
k
S_C^*
S_A
i
ENDO
-20 10 40 70 100 130
T (^{O}C)
(a)
Poly(15-11)
DP
4
5
8
13
15
16
21
k
S_C^*
S_A
i
ENDO
-20 10 40 70 100 130
T (^{O}C)
(b)
Poly(15-11)
DP
4
5
8
13
15
16
21
k
S_C^*
S_A
i
ENDO
-30 0 30 60
T (^{O}C)
(c)

Figure 2.

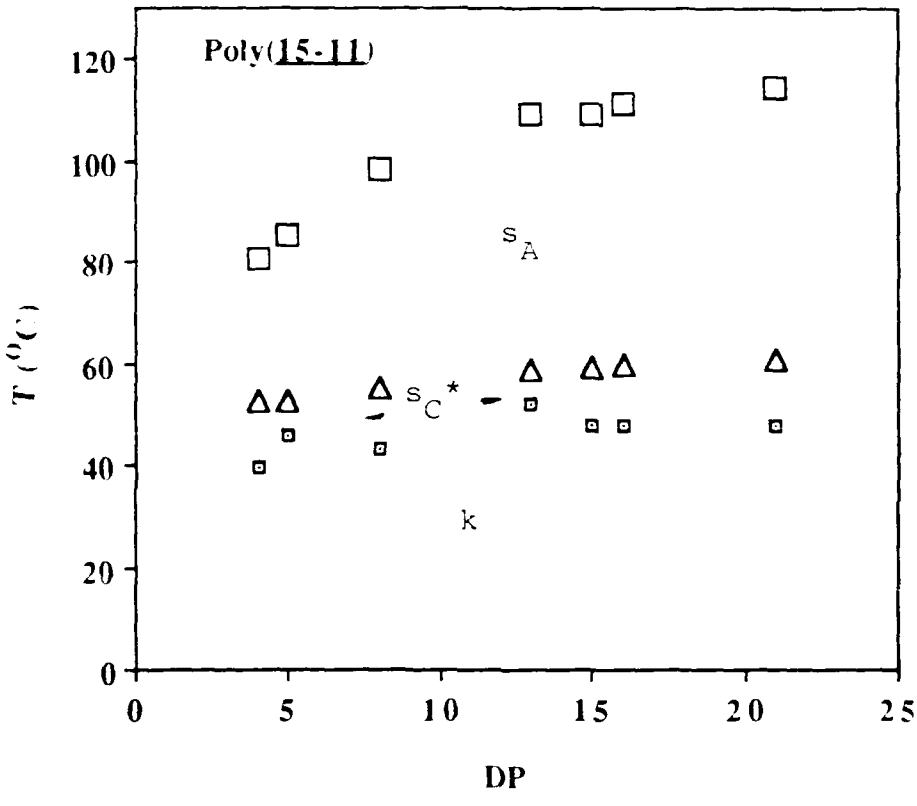


Figure 3. (a)

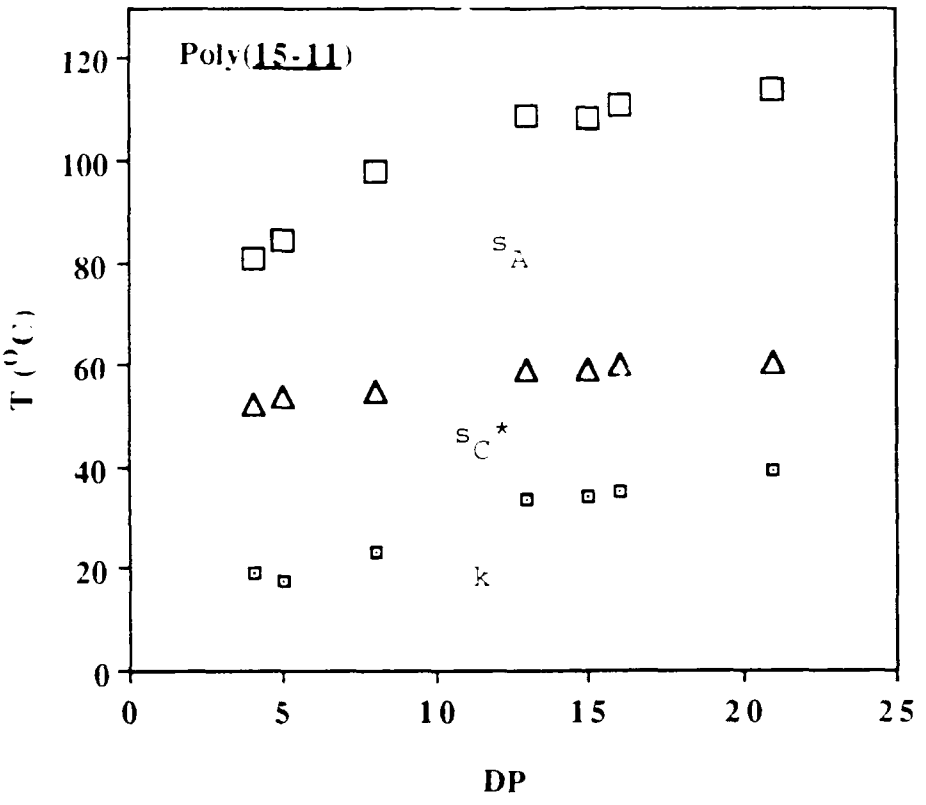


Figure 3. (b)

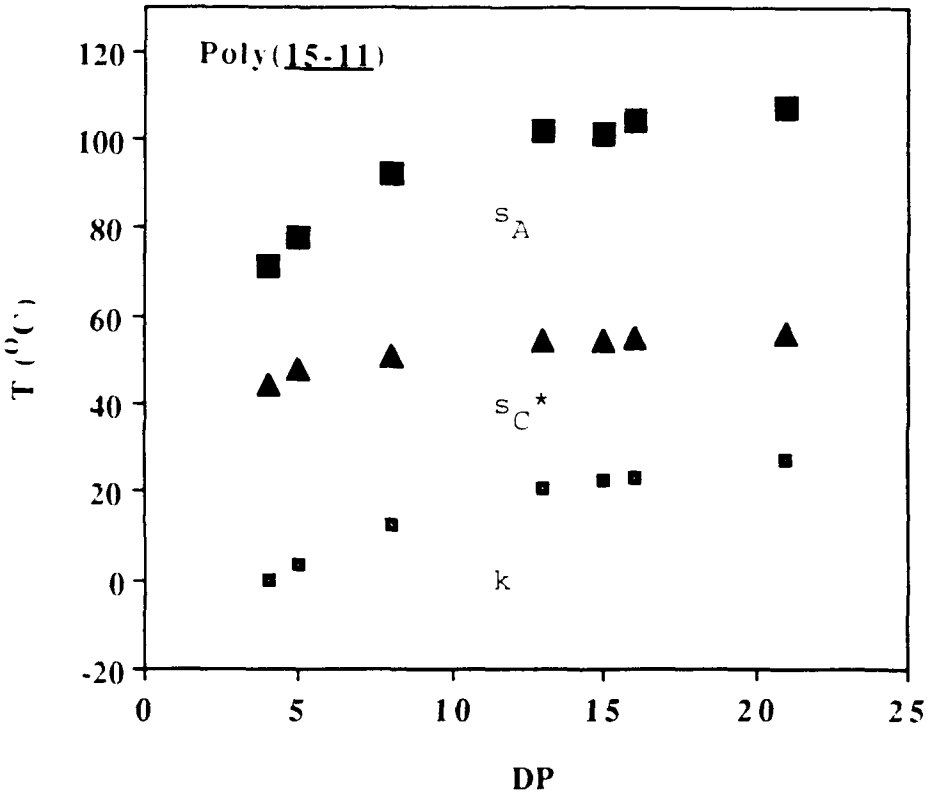


Figure 3. (c)

Figure 4. (a)

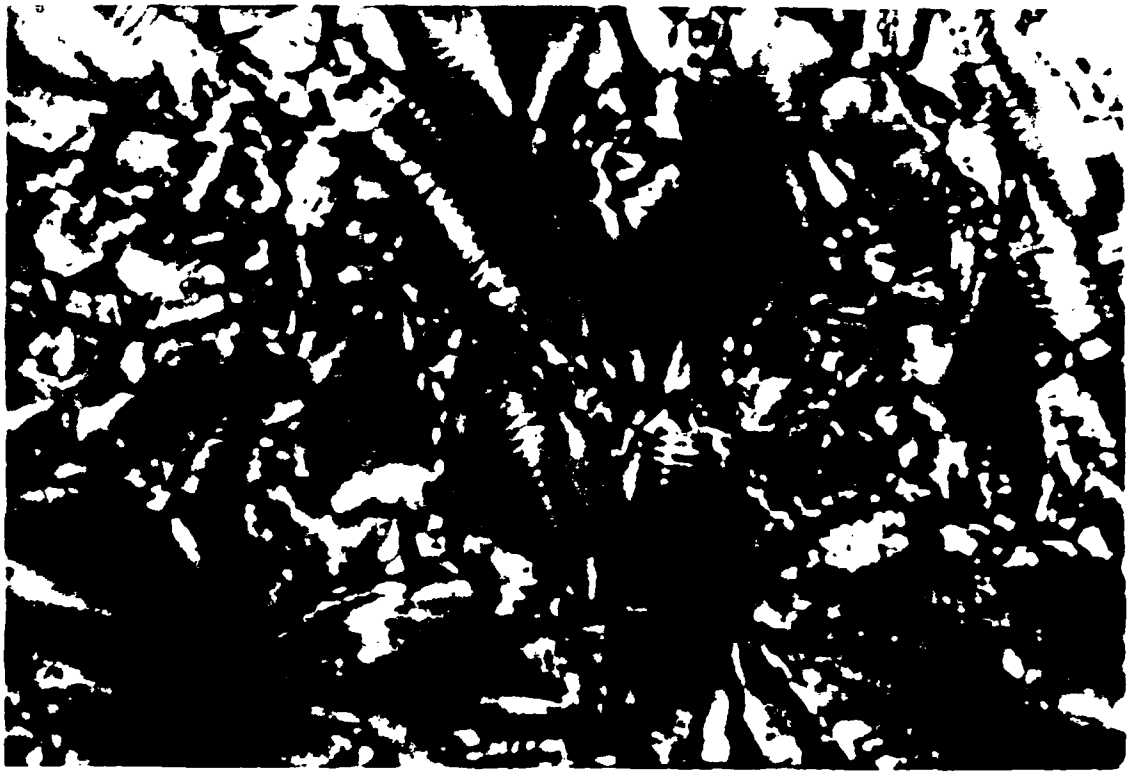


Figure 4. (b)

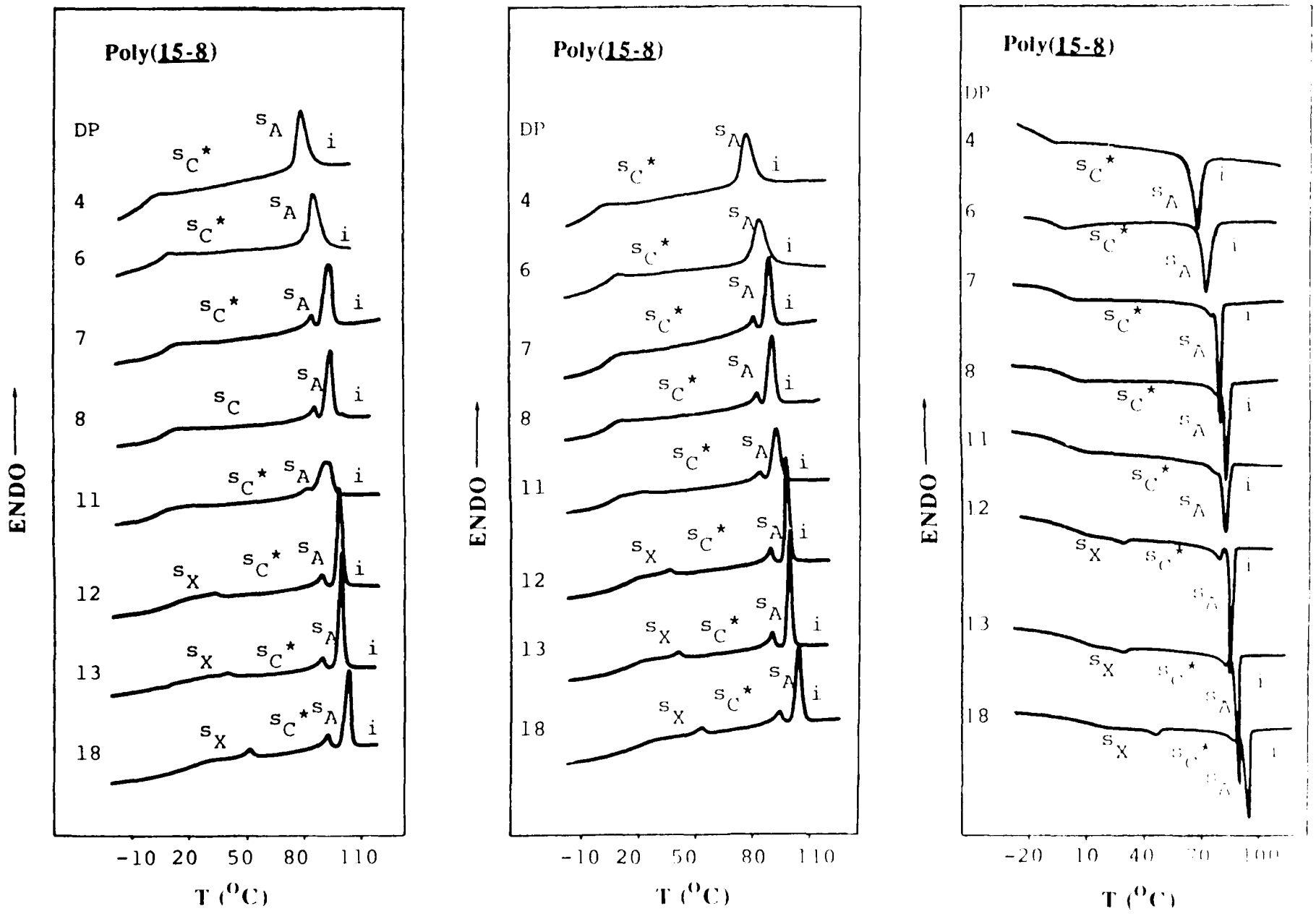

Poly(15-8)
DP
4
6
7
8
11
12
13
18
S_C^*
S_A
S_X
i
ENDO
-10 20 50 80 110
T (°C)
(a)
Poly(15-8)
DP
4
6
7
8
11
12
13
18
S_C^*
S_A
S_X
i
ENDO
-10 20 50 80 110
T (°C)
(b)
Poly(15-8)
DP
4
6
7
8
11
12
13
18
S_C^*
S_A
S_X
i
ENDO
-20 10 40 70 100
T (°C)
(c)

Figure 5.

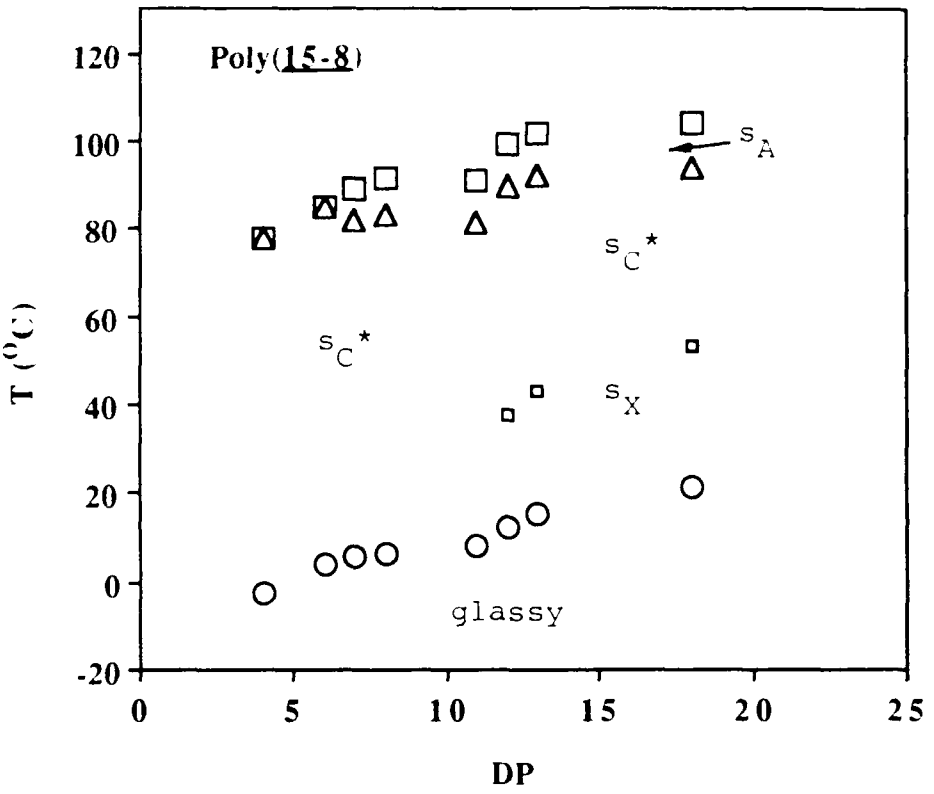

Poly(15-8)
120
100
80
60
40
20
0
-20
T (°C)
0
5
10
15
20
25
DP
s_A
s_C*
s_C*
s_X
glassy

Figure 6. (a)

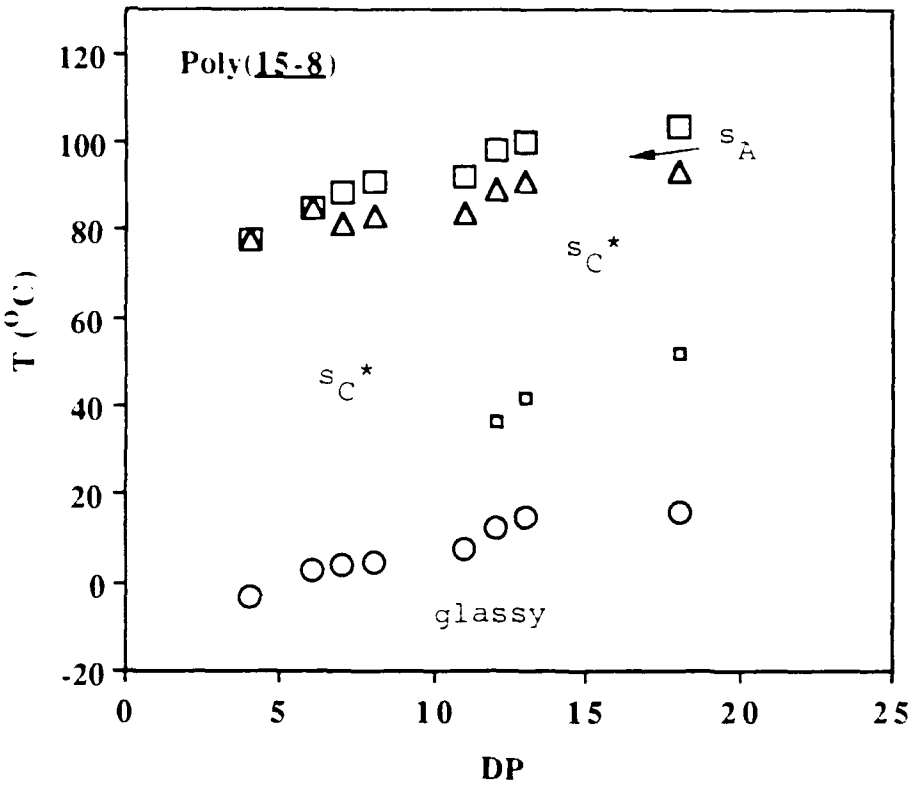

Poly(15-8)
120
100
80
60
40
20
0
-20
T (°C)
0
5
10
15
20
25
DP
S_A
S_C*
S_C*
glassy

Figure 6. (b)

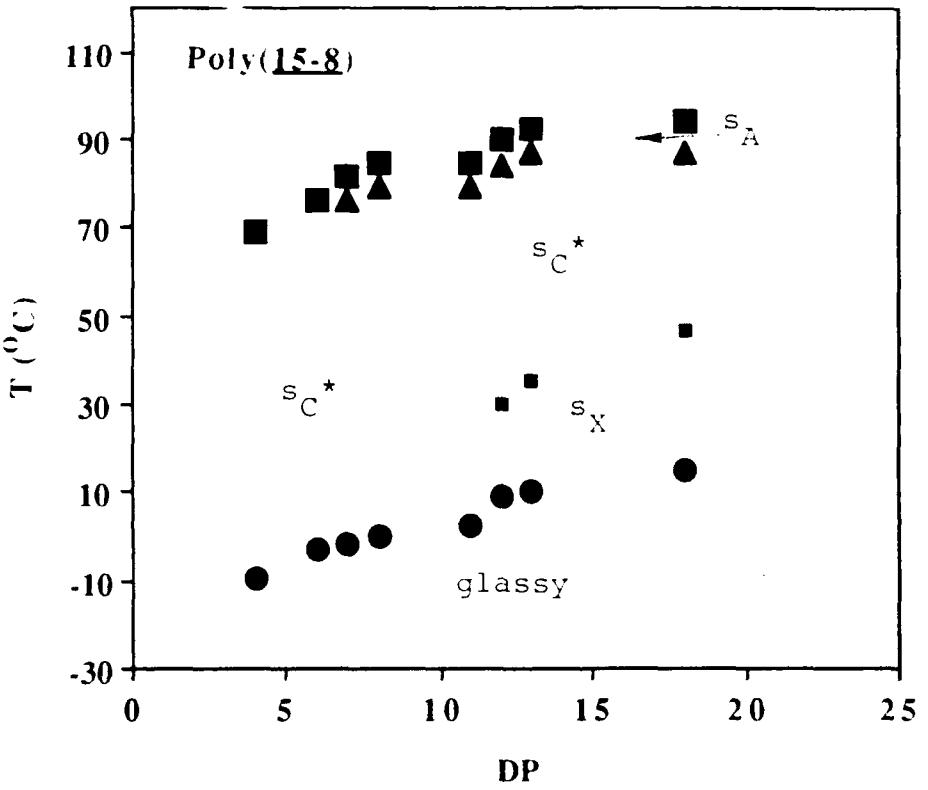

Poly(15-8)
110
90
70
50
30
10
-10
-30
T (°C)
0
5
10
15
20
25
DP
S_A
S_C^*
S_C^*
S_X
glassy

Figure 6. (c)

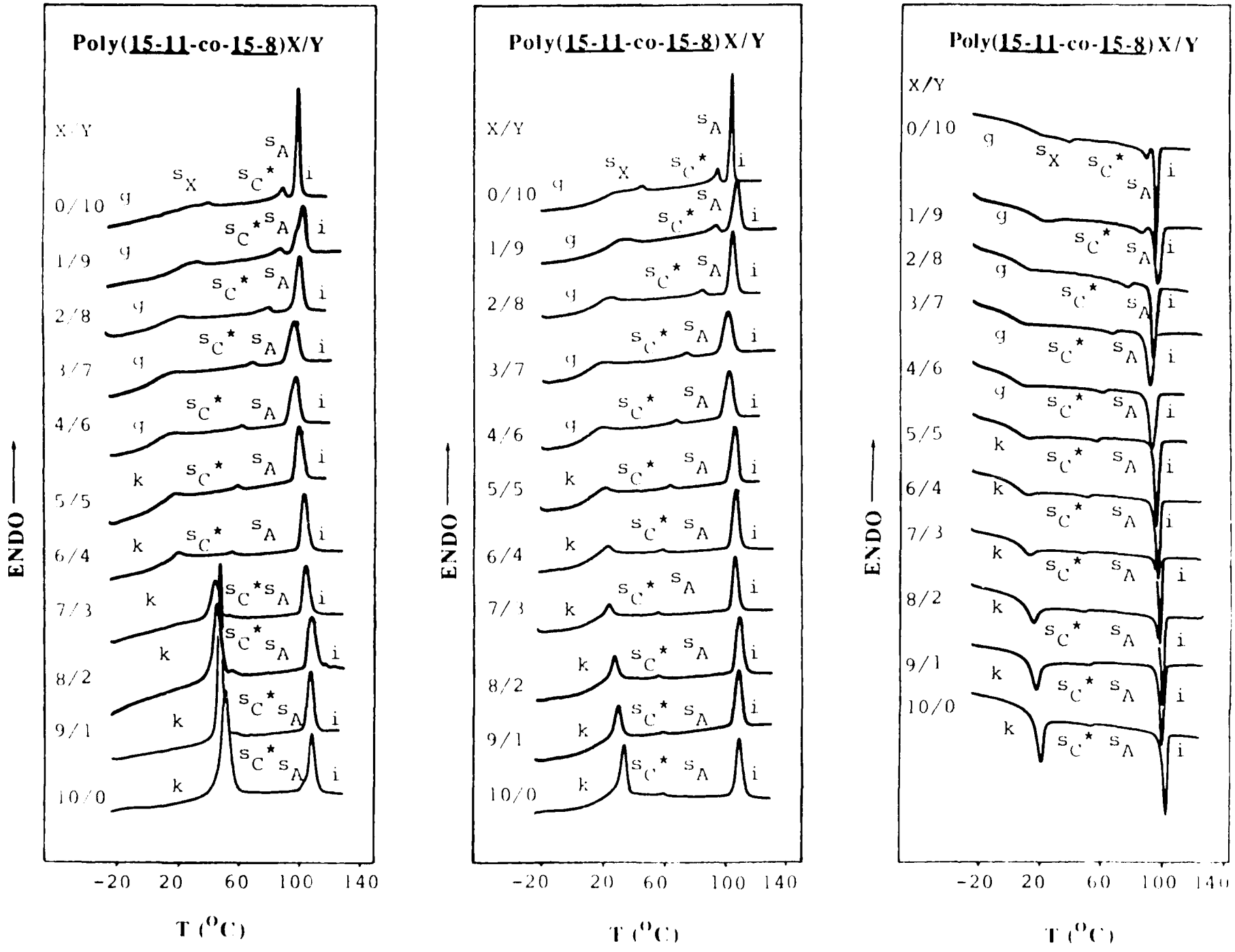

Poly(15-11-co-15-8)X/Y
X/Y
0/10
1/9
2/8
3/7
4/6
5/5
6/4
7/3
8/2
9/1
10/0
g
k
S_X
S_C^*
S_A
i
ENDO
-20
20
60
100
140
T (°C)
(a)
(b)
(c)

Figure 7.

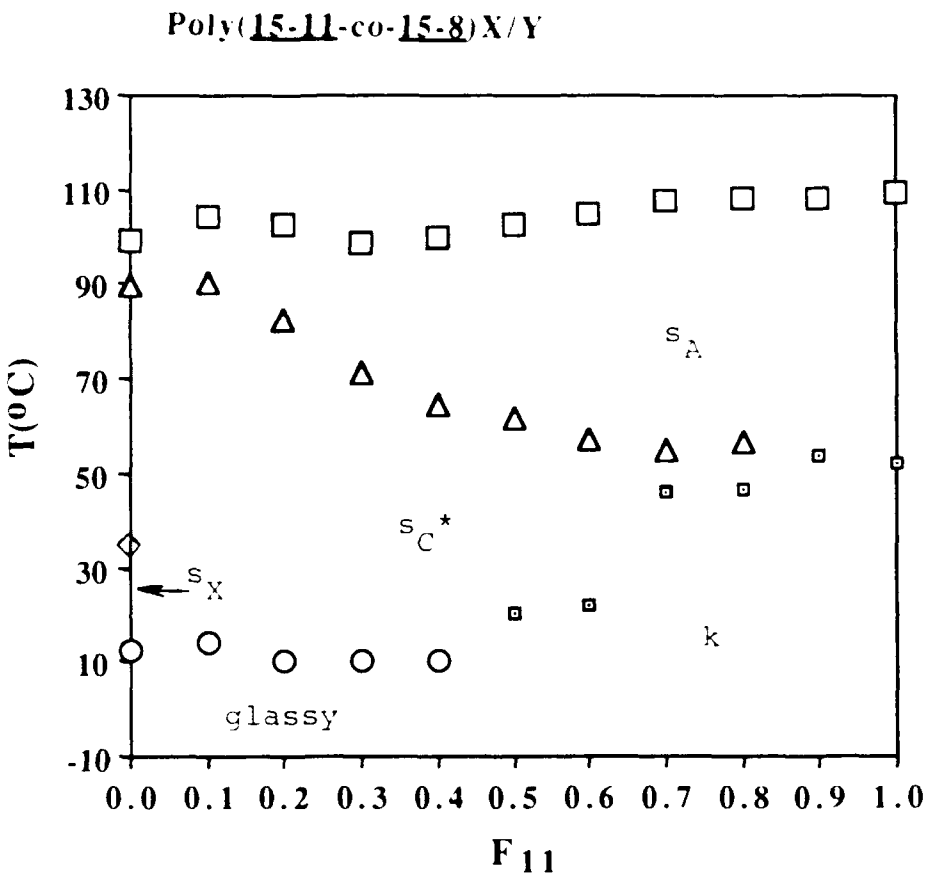

Poly(15-11-co-15-8)X/Y
130
110
90
70
50
30
10
-10
T(°C)
0.0 0.1 0.2 0.3 0.4 0.5 0.6 0.7 0.8 0.9 1.0
F11
S_A
S_C*
S_X
k
glassy

Figure 8. (a)

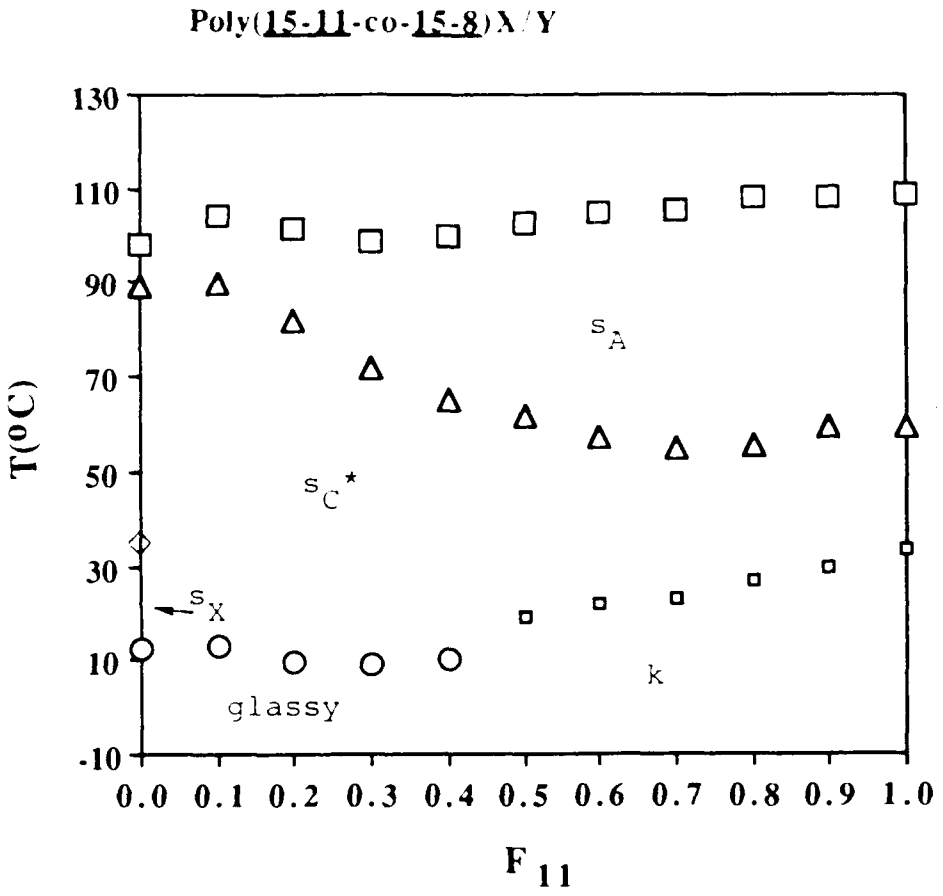

Poly(15-11-co-15-8) X / Y
130
110
90
70
50
30
10
-10
T(°C)
s_A
s_C*
s_X
glassy
k
0.0 0.1 0.2 0.3 0.4 0.5 0.6 0.7 0.8 0.9 1.0
F_{11}

Figure 8. (b)

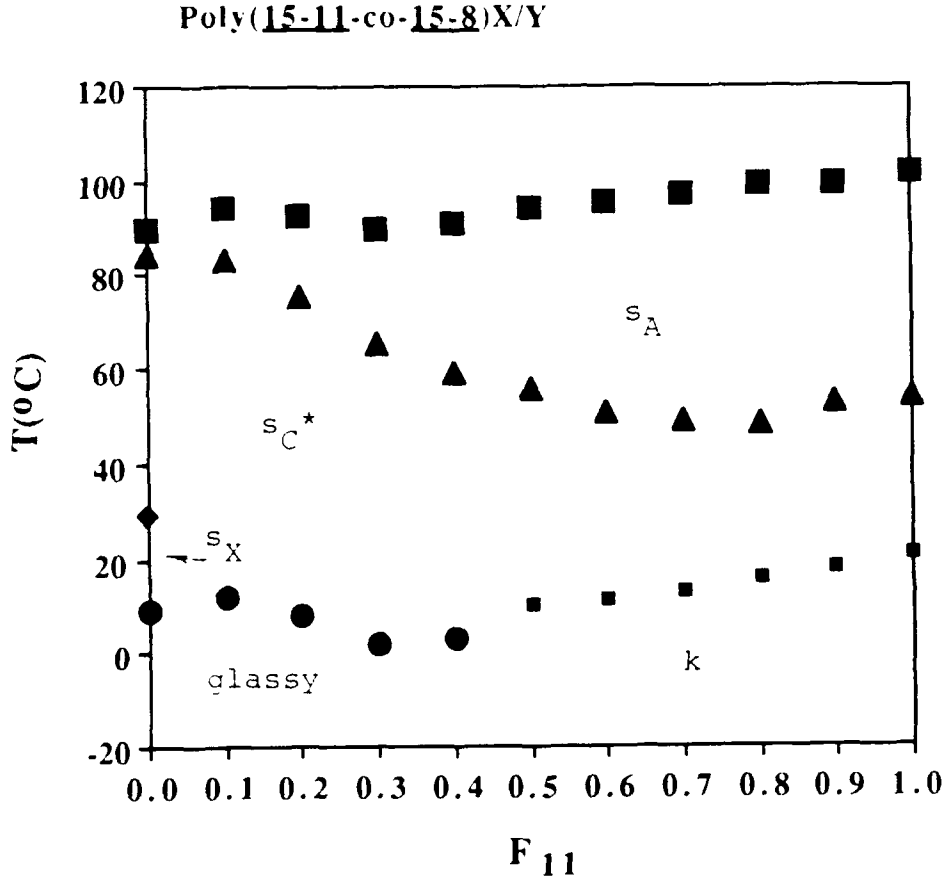

Poly(15-11-co-15-8)X/Y
120
100
80
60
40
20
0
-20
T(°C)
0.0 0.1 0.2 0.3 0.4 0.5 0.6 0.7 0.8 0.9 1.0
F 11
S A
S C*
S X
glassy
k

Figure 8. (c)